PROPERTIES OF SEMICONDUCTING Ru_2Ge_3

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ABSTRACT

Transport properties of large single crystalline samples of Ru_2Ge_3 grown from the melt have been investigated in a 25-1000 C temperature range. A diffusionless transition between 500 and 550 C from a high temperature tetragonal structure to a low temperature orthorhombic structure was clearly observed. Results showed that both the low temperature 01 thorhombic and the high temperature structural tetragonal phase are semiconductors. Some anisotropy of the transport coefficients was determined by measuring the samples in orientations parallel arid perpendicular 10 the preferential direction of crystal growth. Large Seebeck coefficient (up to 400 μVK^{-1}) and low thermal conductivity (as low as $20x10^{-3}$ $Wcm^{-1}K^{-1}$) were achieved for the low temperature orthorhombic phase. Difficulties in preparing heavily doped samples and low Hall nobilities have limited values for the maximum figure of merit to $0.5x10^{-3}K^{-1}$ at 500 C.

INTRODUCTION

Extensive Ihcolc.tics] and experimental studies have resulted in reasonable improvements in the dimensionless figure of merit ZT (up to **50'%)** of the state of the art high temperature thermoelectric $Si_{80}Ge_{20}$ alloys in the last 5 years [1]. 1 lowever, significantly higher material conversion efficiencies are needed to make thermoelectrics competitive and economically attractive. A new approach [2, 3] that looks at radically different compounds and alloys was recently started at the Jet Propulsion Laboratory (J])],). Several Si-rich transition metal silicides with high melting point, complex crystal structure and high density were identified as high temperature semiconductors with good potential for high ZT values [4]. In parallel with the study of Ru_2Si_3, preparation ant{ high temperature transport properties of Ru_2Ge_3 have been investigated at JPI .

Ruthenium sesquigermanide, Ru_2Ge_3, and its isostructural analogs Ru_2Si_3 and Ru_2Sn_3, are known as "chimney-ladder" compounds characterized by long tetragonal unit calls consisting of ß-tin type subcells of Ru atoms stacked one on top of the other, and a helical arrangement of the other Ge, Si or Sn atoms [5]. They have been shown to undergo a diffusionless phase transformation from an orthorhombic centro-symmetric low temperature structure 10 a tetragonal non-centrosymmetric high temperature structure [6]. These transformations, due to short displacements of the Ge, Si or Sn atoms, are reversible and occur gradually over a wide temperature range. Some properties of these compounds were previously investigated by preparing several re-meltings of the elements in RF and arc furnaces until the final products contained only single phase defined by metallography and X-ray powder diffraction analysis [6,'7]. Ru_2Si_3 and Ru_2Ge_3 compounds demonstrated semiconducting pr-opcl-lies wit hhigh temperature modifications energy gaps of 0.44 and 0.34 eV, respectively. These gaps increase discontinuously while the compounds undergo diffusionless phase transformations into the low temperature modifications, Ru_2Ge_3, decomposes peritectically at a temperature of 1 470°C [8], Growth of Ru_2Ge_3 can be achieved by crystallization of slightly off-stoichiometric Ge-rich solutions.

EXPERIMENTAL DETAILS

Growth expel iments with various Ru and Ge compositions showed that good quality single phase Ru_2Ge_3 samples could be obtained from melts containing 38 at. % Ru and 62 at.% Ge [9]. Crystallization from compositions closer to the 2:3 stoichiometric ratio resulted in incisions of RuGe, thus demonstrating that the peritectic plateau of Ru_2Ge_3 extended to 62 at. % (it. Polycrystalline ingots, even with grain cl"oss-sections as large as 5-7 mm, were heavily cracked. I lowever, most of the cracks were located at the grain boundaries, thus the crackless single crystalline grains with dimensions of up to 6x6x3 mm^3 were readily available for investigation. Only completely single crystalline ingots were found to be crack-free. Analyses of Laue patterns taken at ?5 C from such samples (ictcl-mined [1 10] to be the preferential direction of crystal growth [9].

All prepared samples were measured for room temperature Hall effect. Single phase samples of good mechanical strength were also measured for high temperature 1 Iall effect, Seebeck coefficient and thermal conductivity. Because of the complex crystal structure of Ru_2Ge_3, the possible anisotropy of the transport properties had to be taken into account. Most of the thin slices (about 1 mm thick and 1 0mm in diameter) were

horizontal cuts and thus Seebeck and thermal conductivity were measured parallel (||) to the preferential [110] direction of crystal growth while Hall coefficient and electrical resistivity were measured perpendicular (. I) to the [110] direction of crystal growth.

Some Bridgman grown ingots were mechanic.ally strong enough (few cracks) to allow vertical slices to be cut. On these vertical thin slices, Seebeck coefficient and thermal conductivity were measured .I to the [1 IO] direction of crystal growth while Hall coefficient and electrical resistivity were measured || to the [1 1 O] direction of crystal growth. By combining measured propel-lies from both horizontal and vertical cuts located next 10 each other, anisotropy ratios and values for the figure of merit could be calculated for both the || and .1 direction to the [1 10] direction of cryst al growth.

RESULTS AND DISCUSSION

Room temperatur c 1 Hall effect

Measurements, illustrated on Figures 1 and 2, showed that almost all of the investigated samples were of p-type conductivity. Figure 1 shows the decrease in Hall mobility at room temperature with larger earl-icr concentrations, Highest mobility values obtained for undoped samples were about 100 $cm^2V^{-1}s^{-1}$ for a carrier cone.cntlation of $1x10^{17}$ cm^{-3}. The highest purity Ru_2Ge_3 grown fi om a 95 at .% Ge solution had the lowest carrier concentration ($2.4x10^{16}$ cm^{-3}) but the Hall mobility was actually lower (50 $cm^2V^{-1}s^{-1}$). Samples doped with a variety of elements show that the mobility decreases little when increasing carrier concentrations from $1\ 0^{17}$ cm^{-3} up to 10^{19} cm^{-3}, thus effectively lowering the electrical resistivity by almost two orders of magnitude, as seen on Figure 2. However, because mobility values are already low (about 10 (o 40 $cm^2V^{-1}s^{-1}$) the electrical resistivity of these samples still remains one order of magnitude higher than desired (about 20 to $70x10^{-3}$ Ω.cm while state of the art thermoelect ric materials have electrical resistivity values in the 0.5 to 5X103 Ω.cm range).

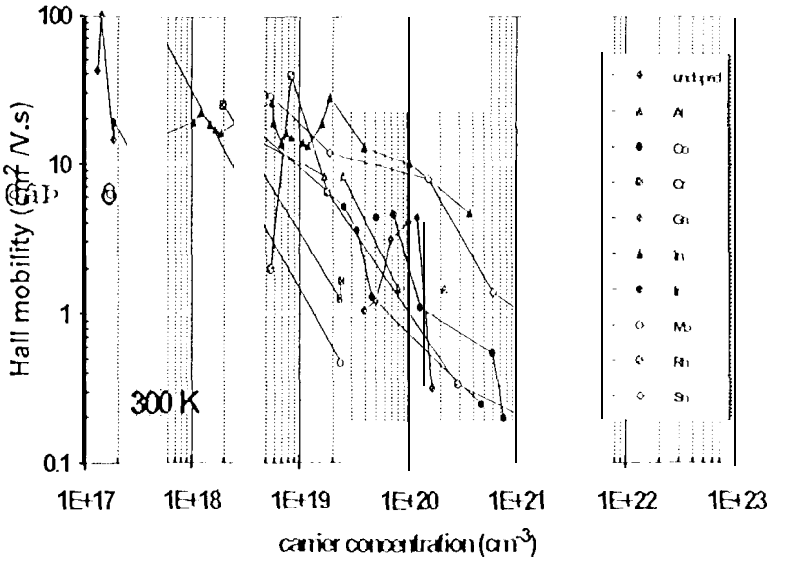

Figure 1 Room temperature Hall mobility versus carrier concentration for doped and undoped Ru_2Ge_3 samples.

Higher dopant concentrations using transition metal elements such as Co, Cr, Ir, Mn, h40, Ni, Pt, Re and Rh either did not succeed in increasing carrier concentrations or resulted in an very fast degradation of the mobility (n^{-1} slope). Figure 2 shows that no gains in electrical resistivity were made for carrier concentrations ranging from 10^{19} cm^{-3} up to 10^{21} cm^{-3}. In contrast, column III elements, Al, Ga and In, as well as Sn were successfully introduced to lower the electrical resistivity value down to 3 to $5x10^{-3}$ Ω.cm.

Using a simple substitutional defect scheme, one would expect Al, Ga, and In to result in p-type conductivity as they replace the Ge in Ru_2Ge_3. However, Ga- arid Al-doped samples were often ofn-type conductivity at room temperature. Similar results were also obtained in samples heavily doped with elements such as Rh, Co or even Sn. Because Hall effect measurements consistently showed high electrical resistivity (> 100 $x10^{-3}$ Ω. cm) and low mobility (< 1-2 $cm^2V^{-1}s^{-1}$), these findings are attributed to one or several of the following mechanisms: a) excess dopant formed second phases (metallic compounds with Ru or Ge exist) of metallic behavior and very poor mobility; b) samples arc compensated, resulting in very small Hall coefficient, high electrical resistivity and thus very low mobility; c) localized levels deep in the band gap have been created; d) n-type carrier mobility is very low. Additional experiments would be required to resolve these findings.

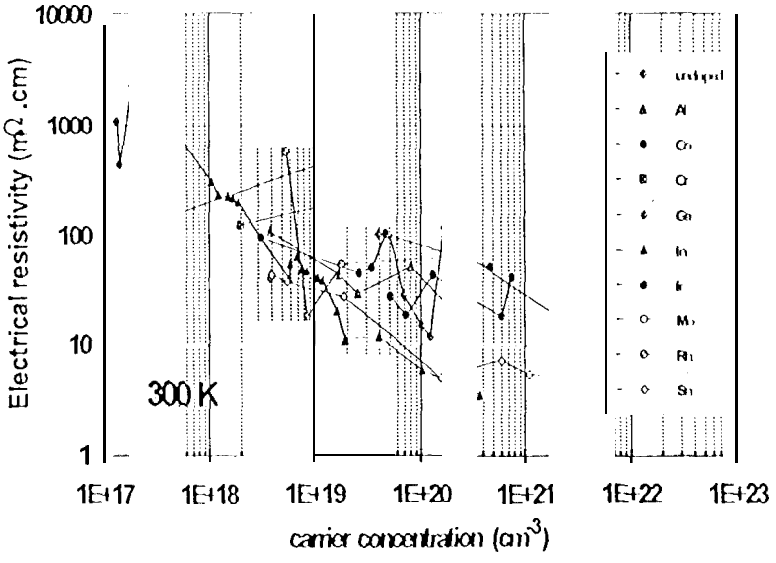

Figure 2 Room temperature electrical resistivity versus carrier concentration for doped and undoped Ru_2Ge_3 samples.

The rationale for the use of Sn was that solid solutions mist between the isostructural Ru_2Ge_3 and Ru_2Sn_3 compounds (at least up to 8 mol.% of Ru_2Sn_3). The Ru_2Sn_3 compound is a very heavily doped semiconductor in its low temperature phase and has metallic behavior in its high temperature phase [7]. Sn additions into Ru_2Ge_3 were likely to produce higher carrier concentrations in the "undoped" solid solution (as WCII as lower thermal conductivity). The lowest electrical resistivity values were obtained in p-type samples doped with nominal amounts of in and Sn in the 1 to 2 at.% range, 1 however, even in these samples t he best mobility values were about 4 to 8 cm^2V^{-1} s-' for carrier concentrations in the 1 0^{20} cm^{-3} range.

High temperature 1 Iall effect

Several good quality Ru_2Ge_3 samples were measured from 1"00111 temperature up to 1000 C. Figure 3 presents electrical resistivity values as a function of the inverse of temperature and Figure 4 plots Hall mobility values as a function of temperature. At the highest temperatures, typical electrical resistivity and Hall mobility values of 2.5x10-3 Ω.cm and 10 $cm^2V^{-1}s^{-1}$ are obtained, regardless of doping levels. This is because the high temperature tetragonal phase has an intrinsic semiconducting behavior, even for the most heavily doped samples prepared in this effort. A bandgap value of 0.58 eV was derived. Below 500 C, the tow temperature orthorhombic structural phase of Ru_2Ge_3 shows that intrinsic behavior is reached for temperatures higher than -400 C.

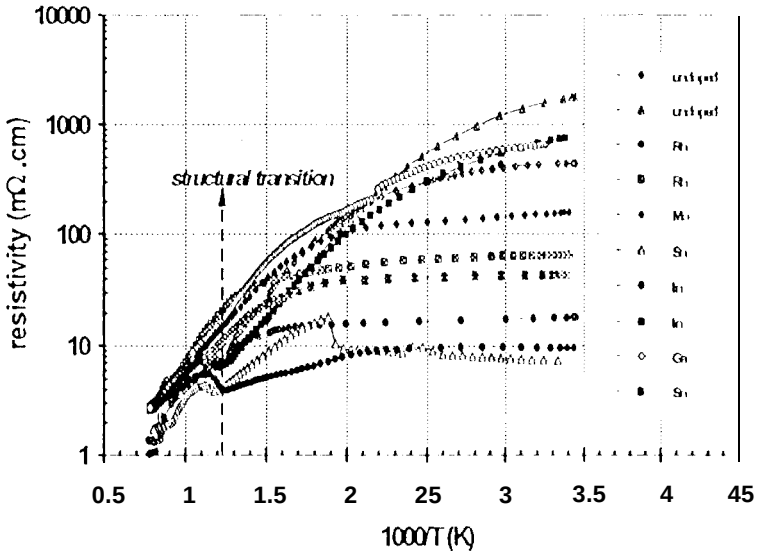

Figure 3 High temperature electrical resistivity versus inverse of temperature for doped and undoped Ru_2Ge_3 samples. Measurements were carried out either || or ⊥ to the [1 10] direction of crystal growth.

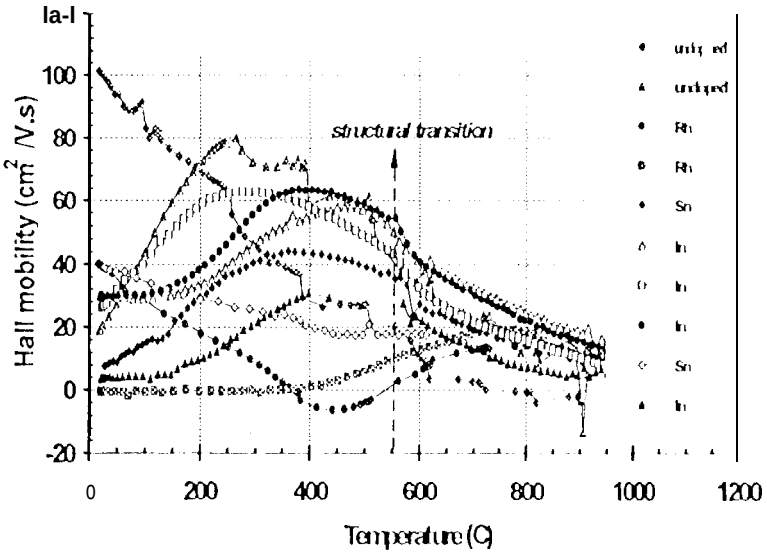

Figure 4 High temperature Hall mobility versus temperature for doped and undoped Ru_2Ge_3 samples. Measurements were carried out either || or ⊥ to the [1 10] direction of crystal growth.

A bandgap value of 0.71 eV was derived from the compared with a value of 0.89 eV determined by photoclc.et] ochemical measurements conducted earlier [9], Samples with the lowest electrical resistivity values did not show any true intrinsic

behavior-. Instead, the straight part of the curve on Figure 3 corresponds 10 the thermal ionization energy of the impurities used for doping Ru_2Ge_3. Similar results can be distinguished albeit with more difficulty on the other curves. Results are displayed in Table 1.

"J'able 1: Thermalionizationenergies

Dopant	Ga	In	Rh
ξ_a (eV)	0.14	0.08	0.05

The increase of Hall mobility with temperature for the low temperature phase indicate that the samples are compensated at room temperature. Because the bandgap is much too large to account for this at mom temperature, these results appear to show that a more complex band structure exists such as deep localized levels, metallic in character, situated in the bandgap. When temperature increases, their contribution diminishes as carriers fill the higher mobility and lower effective mass main valence band. This indicates that the optimum thermoelectric properties of Ru_2Ge_3 will be obtained for the low temperature phase when compensation effects are minimized, that is between 400 and S00 C.

Seebeck coefficient

It is quite remarkable how the variations of the Seebeck coefficient with temperature in Figure 5 are qualitatively similar to those of the Hall mobility in Figure 4. 1 lowever, much larger values are obtained for the Seebeck coefficient than for the mobility for n-type samples. This can be interpreted as n-type earl-icm having large effective masses, thus quenching the mobility but enhancing the Seebeck coefficient. 'J'bus, the beginning of the high temperature intrinsic regime duc to compensation by p-type carriers of significantly lower effective masses would be much more rapid for the 1 Iall mobility than for the Seebeck coefficient. At the lowest temperatures, most samples showed surprisingly low Seebeck values as well as low 1 Iall mobility values. Nearly identical observations were made for Ru_2Si_3 [2, 1 O], Considering the large" bandgap values of 0.72 eV and 1.08 eV of Ru_2Ge_3 and Ru_2Si_3, respectively, it appeared difficult to reconcile cc)llll>c[lsatioll-like effects at low t emperature and intrinsic conduction a t high temperature. Preliminary theoretical attempts working only in terms of several valence and/or conduction bands were not able to reproduce this behavior. This could be explained, as noted before, by the existence of deep localized levels metallic in behavior. Additional data on more heavily doped samples would be required.

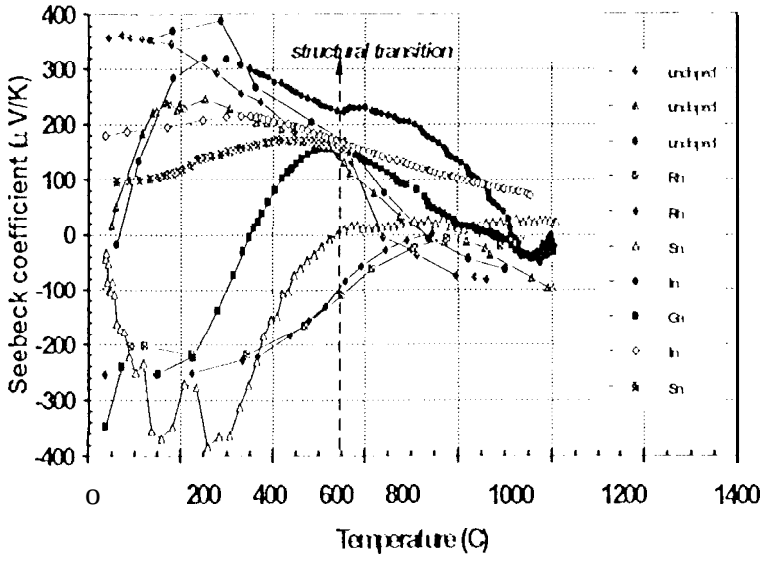

Figure 5 1 ligh t emper at ure Seebeck coefficient versus temper ature for doped and undoped Ru_2Ge_3 samples (measured || toIhc[110] direction of crystal growth).

Still Ru_2Ge_3 is an interesting thermoelectric material as maximum absolute Seebeck values of 400 µV/K can be achieved for both n-type and p-type samples. The low Seebeck values due to intrinsic conduction of the high temperatur c structural phase rule out any hope of achieving high figure of merit values. Best results for Ru_2Ge_3 are to be expected between 200 and 500C.

Thermal conductivity

Thermal conductivity was measured on several samples with various doping levels. The experimental heal capacity value was very slightly larger than the high temperature Dulong-Petit value of 0.297 $Jg^{-1}K^{-1}$. Figure 6 clearly shows that most of the samples had similar thermal conductivity values. A minimum of about $20 \times 10^{-3} W.cm^{-1}.K^{-1}$ at 400 C is obtained for the low temperature orthorhombic phase. This is a low value but it was expected for the complexity of the Ru_2Ge_3 unit cell and the weight of the Ru and Ge elements.

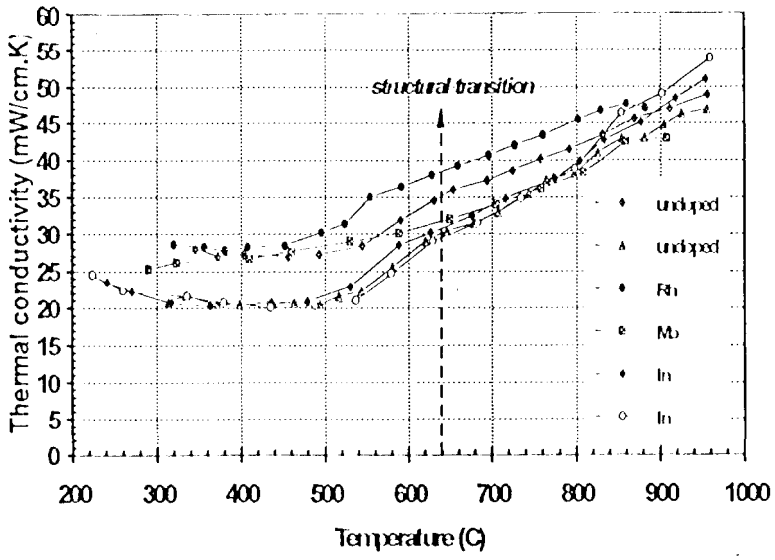

Figure 6 High Impel'allll"c thermal conductivity versus temperature for doped and undoped Ru_2Ge_3 samples (measured|| to the [110] direction of crystal growth).

The electronic contribution (bipolar term due to intrinsic conduction) fully dominates the increase of the thermal conductivity with temperature for the high temperature tetragonal phase. Some of the ingots grown from melts slightly rich in Ge had inclusions of pure Ge. The presence of such inclusions consistently resulted in thermal conductivity 20% higher.

Anisotropic effects and figure of merit

Because of the elongated structure of the orthorhombic Ru_2Ge_3 unit cell, anisotropic transport properties could be expected. Several ingots were cut so that samples could be measured in directions || and .l to the [110] direction of crystal growth. One of the samples (RUGE18 labeled "/" in '1'able 2) was even cut at a 45° angle to the direction of crystal growth to evaluate the results of an average orientation.

Results are reported in '1'able 2 for room temperature Hall effect measurements. Differences in carrier concentration (or hall coefficient) and electrical resistivity are no larger than 50%. For a equivalent carrier concentration, it appears that mobility values in the || orientation are always slightly larger than those in the .l orientation. However, much larger differences in carrier concentration, mobility and electrical resistivity were obtained for sample RUGE16. This could be explained by the fact that RUGE16 samples were large single crystalline plates while the other samples were composed of several grains. Some

disorientation Of these grains would result in average properties and thus less variations between the ⊥ and || cuts.

'J'able ?: Anisotropy of the transport properties of p-type Ru_2Ge_3

Sample 1/	orientation	n	μ_H	P
RUGE16	⊥	3.99X1017	14.46	1083
In-doped	||	$5.79x10^{18}$	26.24	41.0
RUGE17	⊥	$6.91x10^{18}$	14.00	64.6
In-doped	||	$7.58x10^{18}$	16.32	50.5
RUGE18	⊥	$1.05x10^{18}$	19.08	310.3
In-doped	||	$1.67x10^{18}$	17.24	217.4
	/	$1.49x10^{18}$	18.47	226.1
RUG[121	⊥	$3.97x10^{18}$	35.26	44.5
Sn-doped	||	$3.91x10^{18}$	38.46	41.6

Because much larger differences were observed for RUG] ; 16 samples, all their high temperatur c thermoelectric properties were measured. Results are illustrated in Figures 7, 8, 9 and 10. The variations of carrier concentration as a function of the inverse of temperature are displayed on Figure 7. At the beginning of the measurement, t hc carrier concent ration measured in t h e || orientation is about 12 times larger than in the ⊥ orientation However, this difference shrank rapidly as temperature increased (hc.sting curves labeled "h") At 350 C, values in the two orientations are much closer, within 10 to 20°/0. This small difference remained up to 1000 C and back to room temperature (cooling curves labeled "c")

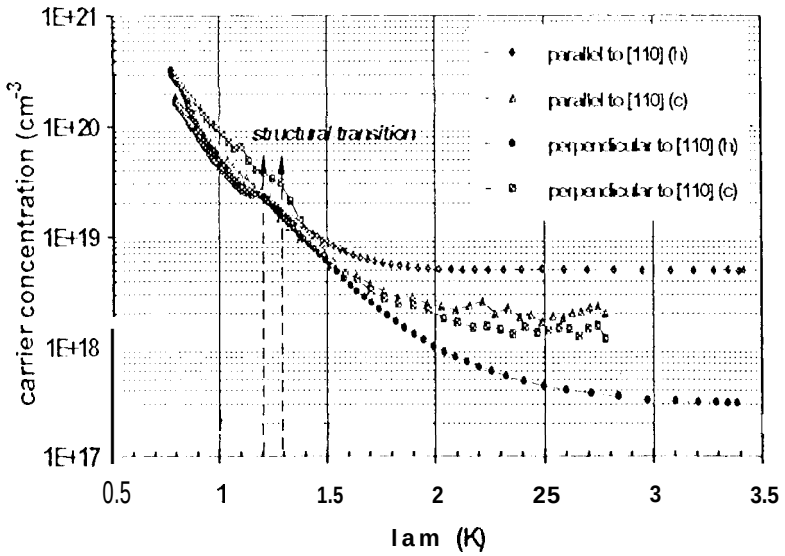

Figure 7 High temperature carrier concentration versus temperature for in-doped Ru_2Ge_3 samples (RUGE16). Measurements || and ⊥ to the [110] direction of crystal growth are compared.

On Figure 8, Hall mobility values for both || and ⊥ orientations are plotted as a function of temperature. Taking into account the simultaneous changes in carrier concentration on Figure 7, the Hall mobility measured in the || orientation is about 50% higher than the mobility measured in the ⊥ orientation. This results in much lower values of the electrical resistivity in the || orientation.

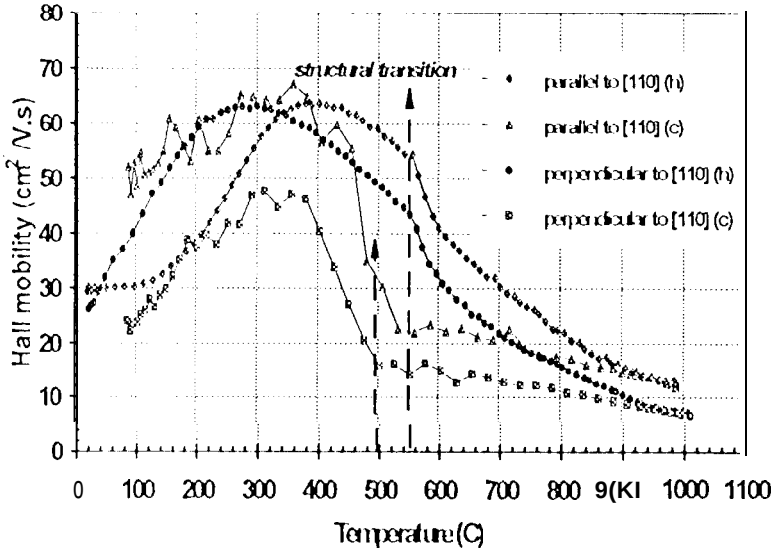

Figure 8 High temperature Hall mobility versus temperature for In-doped Ru_2Ge_3 samples (RUGE16). Measurements || and ⊥ to the [110] direction of crystal growth are compared.

The variations Of the Seebeck coefficient in temperature were found to follow closely those of the mobility (Figure 8), values measured in the || orientation being about 20% higher than the mobility measured in the ⊥ orientation. No significant difference between the || and ⊥ orientations was measured for the thermal conductivity. This was expected since the increase in electronic contribution to the total thermal conductivity due to lower electrical resistivity values in the || orientation was still negligible compared to the lattice thermal conductivity.

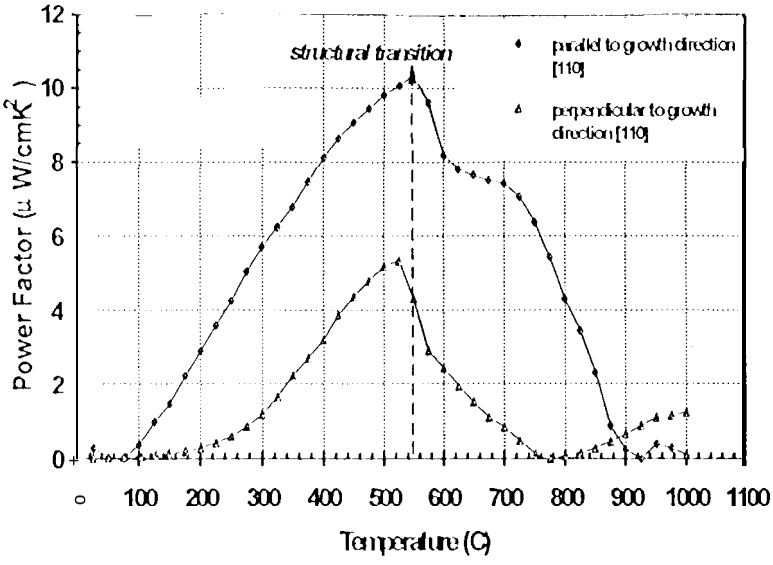

Figure 9 Calculated power factor values versus temperature for In-doped Ru_2Ge_3 samples. Results for directions || and ⊥ to the [110] direction of crystal growth are plotted.

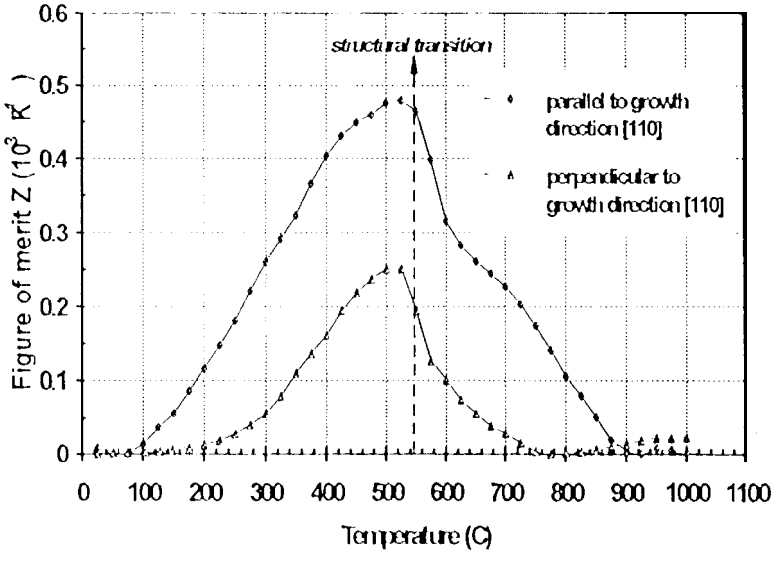

Figure 10 Calculated ZT values versus temperature for In-doped Ru_2Ge_3 samples. Results for directions || and ⊥ to the [110] direction of crystal growth are plotted.

. Some hysteresis was also observed for the structural phase transition. Although its effect on the transport properties was simultaneous in temperature for both the || and ⊥ orientations, it occurred at a temperature close to 550 C upon heating of the

samples and at a temperature slightly below **500 C upon** cooling of the samples (see Figures 7 and 8).

As a consequence of these findings, the best power factor and figure of merit values were obtained || to the preferential direction of crystal growth, as seen on Figures 9 and 10 respectively. A maximum ZT value of about 0.4 was obtained at S00 C along the [1 10] orientation.

CONC1,1JS1ON

The work on Ru_2Ge_3 showed that single crystals of this material could be prepared using unseeded directional crystallization from slightly off-stoichiometric Ge-rich melts. An extensive X-ray analysis determined tile preferential direction of crystal growth as [11 O]. High temperature measurements of the transport properties of doped and undoped Ru_2Ge_3 samples determined that both the high temperature tetragonal phase and the low temperature orthorhombic phase were p-type semiconductors. Bandgap values of about 0,59 eV and 0.71 eV were calculated from Hall effect and electrical resistivity measurements. However, it was found that only the orthorhombic structural phase of Ru_2Ge_3 had a good potential for thermoelectric applications with large Seebeck coefficient (both p-type and n-type) and low thermal conductivity. Unfortunately, the low values of the carrier mobility, the inability to achieve optimum doping levels and the rapid decrease of the mobility with increasing carrier concentration maintained a high electrical resistivity and limited the dimensionless figure of merit to a maximum "experimental" value of 0.4 at 500 C.

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